

*Citation for published version:*

Hall, J, Seeberger, F, Mahon, M & Whittlesey, M 2020, '(carbene)CuF Complexes Featuring Bulky Arduengo-Type, Ring-Expanded, and Cyclic (Alkyl)(amino)carbenes: Applications in Catalytic Aldehyde Allylation', *Organometallics*, vol. 39, no. 1, pp. 227-233. <https://doi.org/10.1021/acs.organomet.9b00772>

*DOI:*

[10.1021/acs.organomet.9b00772](https://doi.org/10.1021/acs.organomet.9b00772)

*Publication date:*

2020

*Document Version*

Peer reviewed version

[Link to publication](#)

**University of Bath**

## **Alternative formats**

If you require this document in an alternative format, please contact:  
[openaccess@bath.ac.uk](mailto:openaccess@bath.ac.uk)

### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

### **Take down policy**

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# (Carbene)CuF Complexes Featuring Bulky Arduengo-Type, Ring-Expanded and Cyclic (Alkyl)(Amino) Carbenes: Applications in Catalytic Aldehyde Allylation

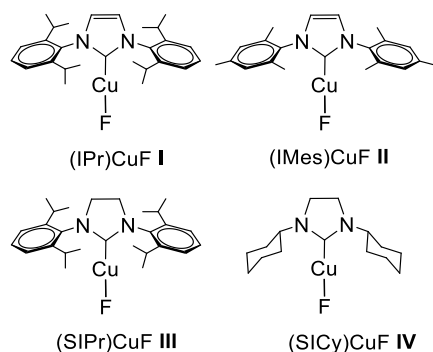
Jonathan W. Hall, Felix Seeberger, Mary F. Mahon, and Michael K. Whittlesey\*

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

**ABSTRACT:** Five examples of two-coordinate copper(I) fluoride complexes stabilized by 5-, 6- and 7-membered ring N-heterocyclic carbenes or a cyclic (alkyl)(amino)carbene have been prepared, structurally characterized and employed in the catalytic allylation of octanal. The very bulky trityl-based carbene ITr affords the most active catalytic system. Mechanistic studies have led to the isolation of (ITr)Cu(CH<sub>2</sub>CHCH<sub>2</sub>) and [ {(6-Mes)Cu}<sub>2</sub>(μ-OEt)][SiF<sub>5</sub>], which along with the fluorosilane (EtO)<sub>3</sub>SiF, are of relevance to the catalytic cycle.

## INTRODUCTION

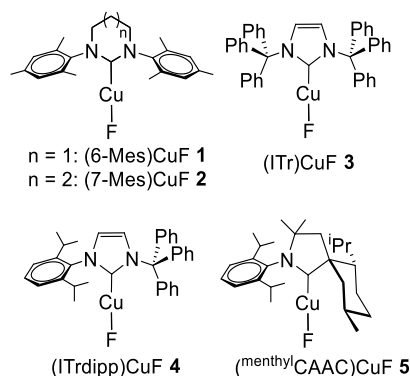
N-heterocyclic carbene (NHC) copper halide complexes represent a simple class of compounds that helped fuel some of the early advances in the application of NHCs as ligands in d-block metal catalysis.<sup>1-7</sup> A considerable number of two-coordinate (NHC)Cu(halide) species have now been prepared which feature not only the well-established Arduengo-type saturated and unsaturated 5-membered ring NHCs, but also less common classes of carbenes, such as ring-expanded (RE-NHCs) and mesionic (or ‘abnormal’) derivatives, triazolyldenes and cyclic (alkyl)(amino) carbenes (CAACs).<sup>8-11</sup> The vast majority of these examples contain the heavier halides, Cl, Br and I, as ligands.



**Chart 1.** Known examples of (NHC)CuF complexes.

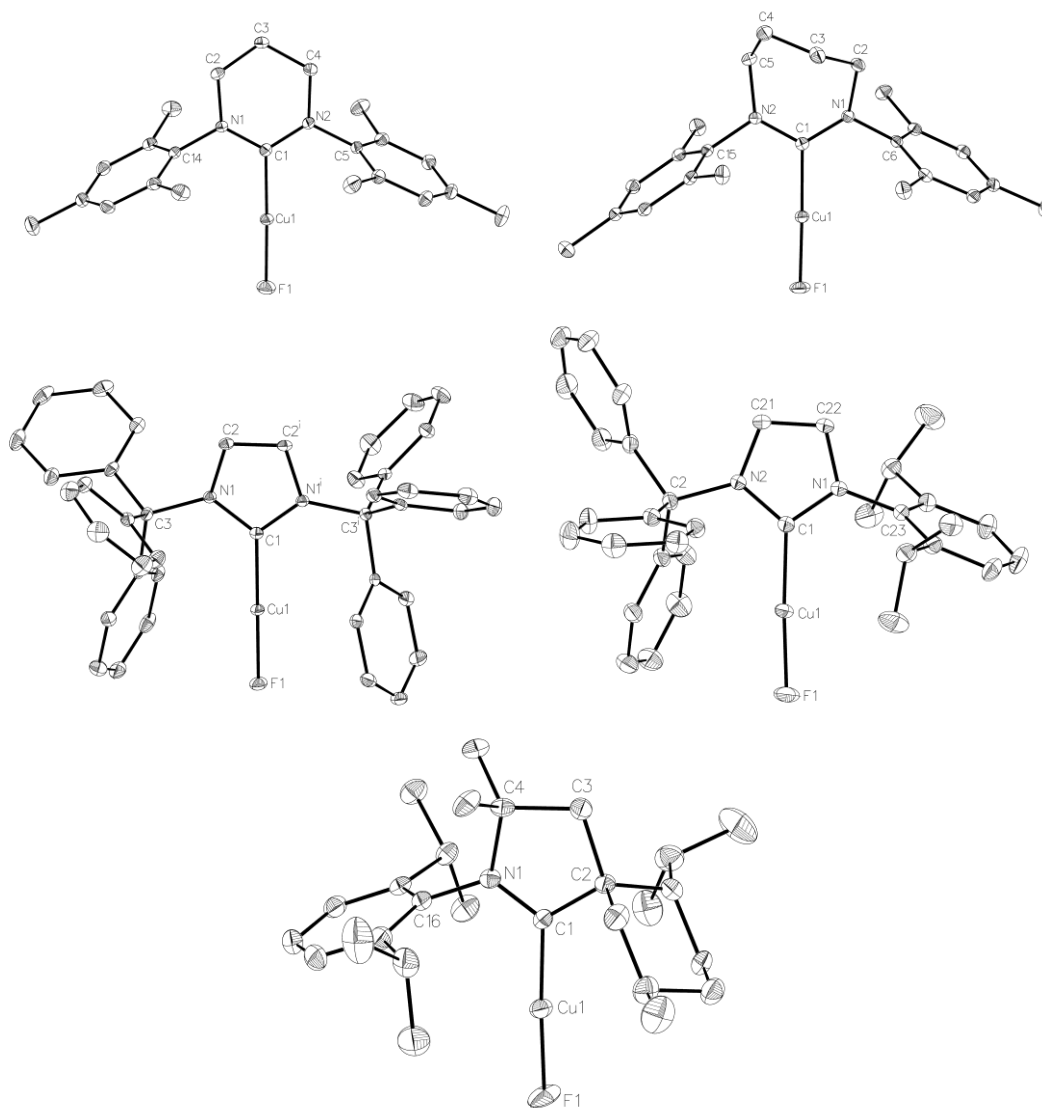
Given the hard-soft mismatch between fluoride and Cu, it seems reasonable to suppose that (NHC)CuF complexes would be of interest in terms of structure/reactivity relationships, as well as in the potential for high activity in the types of catalytic transformations in which (NHC)Cu(halide) complexes have been employed.<sup>12</sup> However, to date, (NHC)CuF

complexes remain scarce. There are only four fully characterized examples in the literature (**I-IV**, Chart 1),<sup>13-16</sup> although these have been shown to exhibit activity in a number of catalytic processes, including alkyne hydrocarboxylation/ hydroxyalkylation,<sup>15,17,18</sup> fluorination of alkyl triflates<sup>19</sup> and aldehyde allylation<sup>20,21</sup> in which the presence of the fluoride group appears to play a key role.<sup>22,23</sup>



**Scheme 1.** New (carbene)CuF complexes.

As complexes **I-IV** all feature quite similar carbenes, our aim was to prepare new examples incorporating a broader array of ligands (Scheme 1). These range from recently developed 5-membered ring NHCs featuring extremely bulky N-CPh<sub>3</sub> substituents<sup>24,25</sup> (**3** and **4**) to ring-expanded (i.e. 6- and 7-membered) derivatives (**1** and **2**).<sup>26</sup> Isolation of the cyclic (alkyl)(amino) carbene (CAAC)<sup>27</sup> derivative **5** is also described. The value of the new carbene ligands has been assessed by comparing the activity of **1-5** to that reported for IPr complex **I** in the catalytic allylation of octanal.<sup>20</sup> Accompanying mechanistic studies have been undertaken.



**Figure 1.** Molecular structures of (left to right, top to bottom) **1-5**. In all cases, ellipsoids are shown at the 30% probability level and hydrogen atoms have been omitted for clarity. In **1**, the structure of the molecule is based on Cu1. In **3**, solvent atoms have been omitted for clarity. Symmetry operation:  $i^{3/2} - x, \frac{1}{2} - y, z$ . In **5**, the structure of the molecule is based on Cu1.

**Table 1. Structural comparison of (carbene)CuF complexes 1-5**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Cu-F (Å)	1.8037(10)	1.7940(11)	1.816(2)	1.7865(10)	1.808(4)
Cu-C <sub>carbene</sub> (Å)	1.8737(15)	1.8647(18)	1.877(4)	1.8525(13)	1.865(5)
C <sub>carbene</sub> -Cu-F (°)	174.30(6)	177.29(7)	180.0	176.34(6)	176.58(18)
%V <sub>bur</sub> <sup>a</sup>	42.7	45.0	62.5	54.6	51.9

<sup>a</sup>Value calculated at M-C<sub>carbene</sub> distance of 2.0 Å. Parameters used: Bondi radii scaled by 1.17, a 3.5 Å sphere radius, 0.1 exhaustiveness and excluding hydrogens.<sup>28</sup>

## RESULTS AND DISCUSSION

Treatment of the corresponding (carbene)CuMes precursors (ESI) with 0.29 equiv  $\text{Et}_3\text{N}\cdot 3\text{HF}$  in THF solution at room temperature gave the desired fluoride complexes (Scheme 1) (6-Mes)CuF (**1**), (7-Mes)CuF (**2**), (ITr)CuF (**3**), (ITrdipp)CuF (**4**) and (<sup>menthyl</sup>CAAC)CuF (**5**) in moderate isolated yields of 62–82%.<sup>29</sup> All five complexes were highly soluble in chlorinated solvents, while **4** and **5** also proved to be soluble in benzene and toluene. The  $^{19}\text{F}$  NMR spectra all exhibited diagnostic low frequency Cu-F resonances in the range  $\delta$  -240 to  $\delta$  -254. For **2–4**, the appearance of a doublet  $^{19}\text{F}$  splitting ( $^2J_{\text{CF}}$  = 32–36 Hz) on the  $^{13}\text{C}$  NMR carbenic resonance confirmed the monomeric nature of the complexes in solution. The carbene signal of **5** appeared as a very broad singlet, while that for **1** could only be characterized by a  $^1\text{H}$ - $^{13}\text{C}$  HSQC.

Single crystals of **1–5** were grown from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  solutions. X-ray diffraction determinations (Figure 1) were consistent with monomeric structures in all cases and revealed close to linear geometries (Table 1).<sup>30</sup> As noted previously by Laitar,<sup>14</sup> meaningful comparisons of Cu-F distances may be limited by the tendency of the fluoride ligand to participate in either hydrogen bonding to solvent or close contacts to neighboring groups. Of the new compounds, only **3** showed evidence of such secondary interactions, with hydrogen bonding to a molecule of dichloromethane. The Cu-F distances were within the range found in **I–IV** (1.8426(10)–1.797(5) Å).

To probe the influence of the different carbene ligands on catalysis, aldehyde allylation was employed as a representative test reaction (Table 2). Herron and Ball reported that the reaction of octanal with trimethoxylallylsilane in the presence of 5 mol% (IPr)CuF (**1**) gave an 85% yield of 1-undecen-4-ol (**6**, Table 2) over 2 days.<sup>20,21</sup> Complexes **1–4** displayed higher levels of reactivity, with high conversions of octanal and high isolated yields of **6** found at only 1 mol% catalyst loading and a 24 h reaction time. CAAC complex **5** showed a disappointing level of activity (Table 2, entry 5). In the case of **1**, benzene was the preferred reaction solvent, with much lower conversion observed in THF (entries 1, 2).

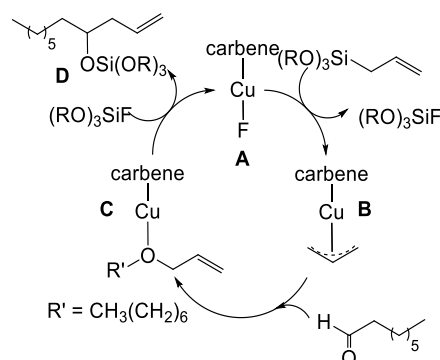
Encouraged by the catalytic results, a series of stoichiometric experiments, alongside additional catalytic reactions, were performed in an effort to probe the catalytic cycle for the allylation reaction. Ball has reported that (IPr)CuF reacts with trimethoxylallylsilane to form (IPr)Cu(CH<sub>2</sub>CHCH<sub>3</sub>) and that this is most likely the species first formed on the catalytic cycle (Scheme 2).<sup>21</sup> Such a (carbene)Cu(allyl) complex (**B**) could then react with aldehyde to afford alkoxide species **C** which, upon reaction with the fluorosilane eliminated in the first step, would yield product **D**, reforming (carbene)CuF complex **A** for propagation of the cycle.

In support of this pathway, ITr complex **3** gave no reaction with octanal, but did react with trimethoxylallylsilane to afford allyl complex **7**. As for the IPr analogue,<sup>21</sup> the allyl ligand was  $\eta^1$ -bound in the solid-state (Figure 2), but exhibited  $\eta^1/\eta^3$  fluxionality in solution (ESI). In the absence of any fluorosilane, **7** was, as expected, catalytically inactive towards the desired product. Upon addition of (EtO)<sub>3</sub>SiF, it showed activity comparable to that of **3**, consistent with formation of allyl complex **B** being the first step on the catalytic cycle (Table 2, entries 8, 9).

**Table 2.** (Carbene)Cu catalyzed allylation of octanal.<sup>a</sup>

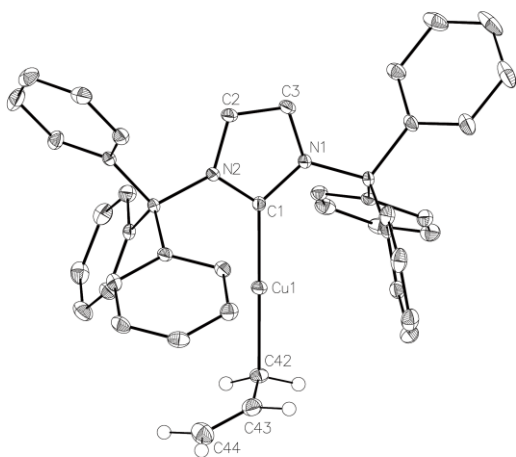
Entry	Precursor	% conv. of octanal <sup>c</sup>	% isolated yield of <b>6</b> <sup>d</sup>
1	<b>1</b>	39 (79)	64
2	<b>1</b> <sup>b</sup>	24 (26)	-
3	<b>2</b>	28 (61)	58
4	<b>3</b>	77 (99)	78
5	<b>4</b>	28 (95)	26
6	<b>5</b>	20 (45)	7
7	-	0 (0)	0
8	<b>7</b>	13 (25) <sup>e</sup>	-
9	<b>7</b> + (EtO) <sub>3</sub> SiF	61 (90)	-
10	(6-Mes)CuO <sup>t</sup> Bu	22 (35) <sup>e</sup>	-
11	(6-Mes)CuO <sup>t</sup> Bu + (EtO) <sub>3</sub> SiF	30 (58)	-
12 <sup>f</sup>	(EtO) <sub>3</sub> SiF	0(0)	-

<sup>a</sup>Conditions: octanal (3 mmol), (carbene)CuF (1 mol%), 1.1 equiv silane, C<sub>6</sub>H<sub>6</sub> (3 mL), 25 °C. <sup>b</sup>THF. <sup>c</sup>Conversions after 4 h (in parentheses, 24 h) determined by  $^1\text{H}$  NMR spectroscopy using 1,3,5-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>3</sub> as an internal standard. <sup>d</sup>Isolated yields following work up after 24 h with *p*-tolylsulfonic acid in MeOH. <sup>e</sup>Conversion of aldehyde was not accompanied by formation of product. <sup>f</sup>5 mol%.

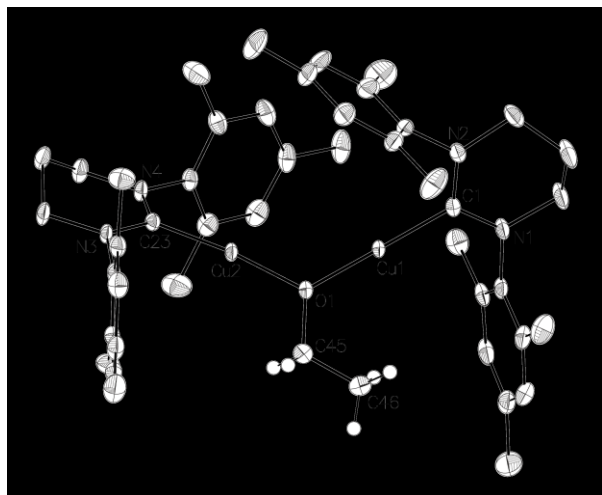


**Scheme 2.** Proposed mechanism for aldehyde allylation.

As an alkoxide complex resulting from the subsequent reaction of **7** with trimethoxylallylsilane proved elusive to isolation, (6-Mes)CuO<sup>t</sup>Bu was employed as a model alkoxide intermediate<sup>31</sup> and, indeed, was found to be catalytically active in the presence of (EtO)<sub>3</sub>SiF (Table 2, entries 10, 11).



**Figure 2.** Molecular structure of (ITr)Cu(CH<sub>2</sub>CHCH<sub>2</sub>) (**7**). Hydrogen atoms, with the exceptions of those in the η<sup>1</sup>-allyl moiety, have been omitted for clarity. Ellipsoids are represented at 30% probability. Selected bond lengths (Å) and angles (°): Cu(1)-C(1) 1.9099(18), Cu(1)-C(42) 1.9587(19), C(42)-C(43) 1.446(3), C(43)-C(44) 1.316(3), C(1)-Cu(1)-C(42) 175.03(9).



**Figure 3.** Molecular structure of the cation in [(6-Mes)Cu]<sub>2</sub>(μ-OEt)[SiF<sub>5</sub>] (**8**). Ellipsoids are shown at 30% probability and hydrogen atoms, with the exceptions of those in the bridging ethoxy moiety, have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)-O(1) 1.8477(16), Cu(2)-O(1) 1.8531(16), Cu(1)-O(1)-Cu(2) 123.27(9).

An accelerating effect of trifluorosilanes on aldehyde allylation has been previously reported.<sup>21,32,33</sup> We observed a similar effect with (6-Mes)CuF **1** in the presence of both **3** and 20 mol% (EtO)<sub>3</sub>SiF, which resulted in complete conversion to product within only 1 h, although for ITr complex **3**, there was no catalytic activity at all at the higher loading. In the absence of any Cu source, (EtO)<sub>3</sub>SiF alone did not catalyse the reaction (Table 2, entry 12).

Much to our surprise, a stoichiometric reaction of (6-Mes)CuO<sup>t</sup>Bu with (EtO)<sub>3</sub>SiF in benzene did not give copper

fluoride product **1** as expected, but instead afforded the ethoxide-bridged copper dimer [(6-Mes)Cu]<sub>2</sub>(μ-OEt)[SiF<sub>5</sub>] (**8**, Figure 3), which precipitated out of the reaction mixture. The same species was also formed upon addition of (EtO)<sub>3</sub>SiF to **1**. The Cu-O distances and Cu-O-Cu angle in **8** are comparable to the values in the μ-hydroxo dicopper cation, [(IPr)Cu]<sub>2</sub>(μ-OH)<sup>+</sup>,<sup>34</sup> as is the long Cu...Cu separation (3.256 Å), which excludes any interaction between the two metal centres.<sup>16a,18,35</sup> Clearly, the presence of the bridging ethoxide ligand, and particularly the [SiF<sub>5</sub>]<sup>-</sup> anion,<sup>36</sup> are consistent with significant degradation of the (EtO)<sub>3</sub>SiF taking place en-route to **8**, although the pathway remains to be established.<sup>33a,37</sup>

The dimer **8** proved to be catalytically active,<sup>18</sup> although preliminary studies have shown that this activity is quite variable, both from one catalytic run to another and also with the order of addition of substrates. Further studies to interrogate this behavior are in hand, as are attempts to probe whether [(NHC)Cu]<sub>2</sub>(μ-OEt)<sup>+</sup> complex formation takes place for all of the (carbene)CuF complexes in Scheme 1 and whether this is a contributing factor to the different activities apparent in Table 2.

## SUMMARY AND CONCLUSIONS

The number of examples of rare (carbene)CuF complexes has been increased with the preparation of the five new derivatives **1-5**, which have been fully characterized both in solution and in the solid-state. Complex **3**, containing the extremely bulky N-CPh<sub>3</sub> substituted carbene ITr, proved to be a very active precursor for the catalytic allylation of octanal. This reaction has been shown to proceed through the intermediacy of the allyl complex (ITr)Cu(CH<sub>2</sub>CHCH<sub>2</sub>) (**7**). Latter stages of the catalytic cycle are less clear cut as a result of the isolation of the unexpected copper dimer in [(6-Mes)Cu]<sub>2</sub>(μ-OEt)[SiF<sub>5</sub>] (**8**) by reaction of (6-Mes)CuO<sup>t</sup>Bu with (EtO)<sub>3</sub>SiF.

## EXPERIMENTAL SECTION

All manipulations were carried out using standard Schlenk, high vacuum and glovebox techniques. Solvents were purified using an MBraun SPS solvent system (hexane, Et<sub>2</sub>O) or under a nitrogen atmosphere from sodium benzophenone ketyl (benzene, THF). NMR solvents were dried (C<sub>6</sub>D<sub>6</sub>/C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> from K, CD<sub>2</sub>Cl<sub>2</sub>/CDCl<sub>3</sub> from CaH<sub>2</sub>) and vacuum transferred. NMR spectra were recorded at 298 K (unless otherwise stated) on Bruker Avance or Agilent 500 MHz NMR spectrometers and referenced to solvent signals as follows: benzene (<sup>1</sup>H, δ 7.16; <sup>13</sup>C{<sup>1</sup>H}, δ 128.0), CD<sub>2</sub>Cl<sub>2</sub> (δ 5.32; δ 54.0), CDCl<sub>3</sub> (δ 7.24; δ 77.2), C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> (<sup>1</sup>H, δ 2.09; <sup>13</sup>C{<sup>1</sup>H}, δ 20.4). Resonances annotated with \* were assigned using <sup>13</sup>C-<sup>1</sup>H HMBC experiments. <sup>19</sup>F NMR spectra were referenced externally to CFCl<sub>3</sub> (δ 0.0). Elemental analyses were performed by Elemental Microanalysis Ltd, Okehampton, Devon, UK. Et<sub>3</sub>N·3HF (Sigma) was used as received. (6-Mes)CuMes and (7-Mes)CuMes were prepared according to the literature.<sup>38,39</sup>

**(6-Mes)CuF (1).** Et<sub>3</sub>N·3HF (46.5 μL, 0.29 mmol) was added to a stirred benzene solution (5 mL) of (6-Mes)CuMes (495 mg, 0.99 mmol) to afford a colorless precipitate within 5 min. After stirring for a further 1 h, the precipitate was filtered, washed with C<sub>6</sub>H<sub>6</sub> (2 × 3 mL) and dried in vacuo to yield **1** as an off-white powder. Yield 230 mg (66%). Crystals suitable for X-ray diffraction were obtained from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. **1** could also be obtained upon reaction of (6-Mes)CuO<sup>t</sup>Bu with Et<sub>3</sub>N·3HF. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.01 (s, 4H, *m*-CH), 3.35 (t, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, 4H, NCH<sub>2</sub>CH<sub>2</sub>), 2.23 (m, 20H, *o*/*p*-CH<sub>3</sub> + NCH<sub>2</sub>CH<sub>2</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  201.0 (s, NCN), \* 142.6 (s), 138.1 (s), 134.8 (s), 129.7 (s), 44.3 (s), 20.9 (s), 20.8 (s), 17.8 (s).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -244.6 (s).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -252.4 (s). Elemental analysis calcd (%) for  $\text{C}_{22}\text{H}_{28}\text{N}_2\text{FCu}$  (403.00): C, 65.56; H, 7.00; N, 6.95; found C, 65.22; H, 7.03; N, 6.88.

**(7-Mes)CuF (2).** As for **1**, using (7-Mes)CuMes (260 mg, 0.5 mmol) and  $\text{Et}_3\text{N}\cdot 3\text{HF}$  (23.5  $\mu\text{L}$ , 0.15 mmol) to yield **2** as an off-white solid. Yield 123 mg (66% yield).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.90 (s, 4H, *m-CH*), 3.85 (m, 4H,  $\text{NCH}_2\text{CH}_2$ ), 2.35 (s, 12H, *o-CH*), 2.29–2.20 (m, 10H, *p-CH* +  $\text{NCH}_2\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  211.4 (d,  $J_{\text{CF}} = 36$  Hz, NCN), 144.6 (s), 137.9 (s), 134.1 (s), 130.2 (s), 52.6 (s), 25.7 (s), 21.2 (s), 18.7 (s).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -253.8 (s). Elemental analysis calcd (%) for  $\text{C}_{23}\text{H}_{30}\text{N}_2\text{FCu}$  (417.02): C, 66.24; H, 7.25; N, 6.72; found C, 65.98; H, 7.23; N, 6.71.

**(ITr)CuF (3).** As for **1** using (ITr)CuMes (ESI; 648 mg, 0.881 mmol) and  $\text{Et}_3\text{N}\cdot 3\text{HF}$  (45  $\mu\text{L}$ , 0.278 mmol) to yield **3** as an off-white solid. Yield 365 mg of **3** (69%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32–7.27 (m, 18H,  $\text{CH}_{\text{aryl}}$ ), 7.25–7.20 (m, 12H,  $\text{CH}_{\text{aryl}}$ ), 6.96 (s, 2H,  $\text{NCH}=\text{CHN}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.0 (d,  $J_{\text{CF}} = 32$  Hz, NCN), 142.4 (s), 130.1 (s), 128.2 (s), 128.1 (s), 120.2 (s), 78.1 (s).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -251.4 (s). Elemental analysis calcd (%) for  $\text{C}_{41}\text{H}_{32}\text{N}_2\text{FCu}\cdot 2\text{CH}_2\text{Cl}_2$ : C, 64.15; H, 4.51; N, 3.48; found C, 63.96; H, 4.53; N, 3.62.

**(ITrDipp)CuF (4).**  $\text{Et}_3\text{N}\cdot 3\text{HF}$  (13  $\mu\text{L}$ , 0.082 mmol) was added to a stirred  $\text{C}_6\text{H}_6$  suspension (5 mL) of (ITrDipp)CuMes (ESI; 170 mg, 0.26 mmol) to afford a yellow/brown solution. After stirring for 1 h, the solution was filtered, concentrated and precipitated by addition of  $\text{Et}_2\text{O}$  to give an off-white solid. Precipitation with  $\text{Et}_2\text{O}$  from benzene was performed twice to yield **4** as an off-white powder (112 mg, 82%). Analytically clean compound was obtained from  $\text{CH}_2\text{Cl}_2$ /pentane.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41–7.31 (m, 16H,  $\text{CH}_{\text{aryl}}$ ), 7.23–7.16 (m, 3H,  $\text{CH}_{\text{aryl}}$  +  $\text{NCH}=\text{CNH}$ ), 6.86 (d,  $J_{\text{HH}} = 1.2$  Hz, 1H,  $\text{NCH}=\text{CNH}$ ), 2.41 (sept,  $J_{\text{HH}} = 6.9$  Hz, 2H,  $\text{CHMe}_2$ ), 1.22 (d,  $J_{\text{HH}} = 6.9$  Hz, 6H,  $\text{CHMe}_2$ ), 1.15 (d,  $J_{\text{HH}} = 6.9$  Hz, 6H,  $\text{CHMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ):  $\delta$  184.3 (d,  $J_{\text{CF}} = 33$  Hz, NCN), 145.4 (9s), 142.5 (s), 135.7 (s), 130.3 (s), 130.2 (s), 128.5 (s), 128.4 (s), 124.3 (s), 122.4 (s), 121.2 (s), 77.9 (s), 28.7 (s), 24.8 (s), 24.0 (s).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -250.4 (s). Elemental analysis calcd (%) for  $\text{C}_{34}\text{H}_{34}\text{N}_2\text{FCu}$ : C, 73.82; H, 6.20; N, 5.06; found C, 73.90; H, 6.08; N, 5.08.

**( $^{\text{menthyl}}$ CAAC)CuF (5).**  $\text{Et}_3\text{N}\cdot 3\text{HF}$  (36  $\mu\text{L}$ , 0.22 mmol) was added to a stirred  $\text{Et}_2\text{O}$  (5 mL) solution of ( $^{\text{menthyl}}$ CAAC)CuMes (ESI; 391 mg, 0.69 mmol) to give a colorless precipitate. After 1 h, the suspension was filtered, the precipitate washed with  $\text{Et}_2\text{O}$  (2 x 10 mL) and dried in vacuo to yield **5** as an off-white powder. Yield 190 mg (62 %).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.44 (t,  $J = 7.7$  Hz, 1H,  $\text{CH}_{\text{aryl}}$ ), 7.33–7.28 (m, 2H,  $\text{CH}_{\text{aryl}}$ ), 2.94–2.78 (m, 2H), 2.75–2.61 (m, 2H), 2.29 (d,  $J = 13.7$  Hz, 1H), 2.14–2.06 (m, 1H), 1.98–1.81 (m, 3H), 1.77 (d,  $J = 13.7$  Hz, 1H), 1.43–1.27 (m, 17H), 1.24 (d,  $J_{\text{HH}} = 6.6$  Hz, 3H,  $\text{CH}(\text{CH}_3)$ ), 1.16–0.99 (m, 7H), 0.90 (d,  $J_{\text{HH}} = 6.5$  Hz, 3H,  $\text{CH}(\text{CH}_3)$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  250.9 (br s, NCC), 160.0 (s), 145.6 (s), 136.2 (s), 129.9 (s), 125.3 (s), 125.1 (s), 77.8 (s), 65.4 (s), 52.8 (s), 51.5 (s), 48.9 (s), 36.1 (s), 31.4 (s), 30.0 (s), 29.6 (s), 29.6 (s), 29.4 (s), 28.1 (s), 27.8 (s), 26.8 (s), 25.4 (s), 24.5 (s), 22.9 (s), 22.6 (s), 22.5 (s), 20.2 (s).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -240.0 (s).  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ ):  $\delta$  -245.1 (s). Elemental analysis calcd (%) for  $\text{C}_{27}\text{H}_{43}\text{NFCu}$  (463.27) C, 69.86; H, 9.34; N, 3.02; found C, 69.93; H, 9.27; N, 3.26.

**(ITr)Cu(CH<sub>2</sub>CHCH<sub>2</sub>) (7).** Trimethoxylallylsilane (31  $\mu\text{L}$ , 0.18 mmol) was added to a stirred benzene solution (10 mL) of **3** (115 mg, 0.18 mmol) to afford a bright yellow solution. After 1 h, the solution was filtered, concentrated and pentane added to afford a colorless precipitate. This was collected, washed with cold pentane (2 x 5 mL) and dried under vacuum to give **7** as an off-white powder. Yield 43 mg (36 %). Crystals suitable for X-ray diffraction were obtained from  $\text{Et}_2\text{O}$ /pentane at -30 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta$  7.30–7.25 (m, 12H), 7.11–7.06 (m, 14H), 7.05–7.02 (m, 4H), 6.54 (s, 2H), 5.83 (quint,  $J_{\text{HH}} = 11.1$  Hz, 1H), 2.39 (d,  $J_{\text{HH}} = 11.1$  Hz, 4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta$  192.6 (s, NCN), 150.3 (s), 143.4 (s), 130.4 (s), 128.0 (s), 127.7 (s), 119.1 (s), 78.1 (s), 57.7 (br s). Efforts to determine

elemental analysis (%) for  $\text{C}_{44}\text{H}_{37}\text{N}_2\text{Cu}$  (657.30) gave consistently low %C (e.g. calcd C, 80.40; H, 5.67; N, 4.26; found C, 78.03; H, 5.45; N, 4.20).

**{[(6-Mes)Cu]<sub>2</sub>( $\mu$ -OEt)[SiF<sub>3</sub>]} (8).** Triethoxyfluorosilane (176  $\mu\text{L}$ , 0.947 mmol) was added to a stirred benzene suspension (10 mL) of **1** (150 mg, 0.316 mmol) to afford a colorless solution. After <5 min, the solution yielded a colorless precipitate, which was isolated by filtration, redissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL) and then reprecipitated via addition of pentane. After isolation by filtration, the solid was washed with pentane (2 x 5 mL) and dried in vacuo to yield an off-white powder. Yield 120 mg (81 %). Crystals suitable for X-ray diffraction were obtained from  $\text{CH}_2\text{Cl}_2$ /pentane.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 272 K):  $\delta$  6.89 (s, 8H, *m-CH*), 3.25 (t,  $J_{\text{HH}} = 5.9$  Hz, 8H,  $\text{NCH}_2\text{CH}_2$ ), 2.37 (br quart, 2H,  $\text{OCH}_2$ ); 235 K:  $\delta$  2.33 (quart,  $J_{\text{HH}} = 6.9$  Hz), 2.28 (s, 12H, *p-CH*), 2.23 (q,  $J_{\text{HH}} = 5.9$  Hz, 4H,  $\text{NCH}_2\text{CH}_2$ ), 2.12 (s, 24H, *o-CH*), 0.07 (br t,  $J_{\text{HH}} = 7.1$  Hz, 3H,  $\text{OCH}_2\text{CH}_3$ ); 235 K:  $\delta$  -0.04 (t,  $J_{\text{HH}} = 6.9$  Hz).  $^{19}\text{F}$  (376 MHz,  $\text{CD}_2\text{Cl}_2$ , 235 K):  $\delta$  -138.9 (s;  $J_{\text{FSi}} = 147$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ , 272 K):  $\delta$  199.1 (s, NCN), 142.3 (s), 138.2 (s), 134.8 (s), 129.7 (s), 63.6 (br s), 44.5 (s), 22.6 (br s), 21.1 (s), 20.9 (s), 18.0 (s). Elemental analysis calcd (%) for  $\text{C}_{46}\text{H}_{61}\text{N}_4\text{O}_5\text{SiCu}_2\cdot 0.75\text{CH}_2\text{Cl}_2$  (999.86; ESI): C, 56.15; H, 6.30; N, 5.60; found C, 56.09; H, 6.33; N, 5.67.

**Catalytic allylation of octanal with (carbene)CuF precursors.** (i) *NMR scale reactions:* To a  $\text{C}_6\text{D}_6$  (1 mL) suspension of **1-5** (1 mol%) and 1,3,5-trimethoxybenzene reference (56 mg, 0.33 mmol) in a J. Youngs NMR tube was added octanal (156  $\mu\text{L}$ , 1.0 mmol) followed by trimethoxylallylsilane (185  $\mu\text{L}$ , 1.1 mmol, 1.1 equiv). The reaction mixture was shaken at room temperature and monitored by NMR spectroscopy. (ii) *Preparative scale reactions:* Under the argon atmosphere of a glovebox, a  $\text{C}_6\text{H}_6$  (3 mL) suspension of **1-5** (1 mol%) in a screw cap vial equipped with a PTFE stirrer bar was added octanal (468  $\mu\text{L}$ , 3.0 mmol) followed by trimethoxylallylsilane (185  $\mu\text{L}$ , 3.3 mmol, 1.1 equiv). After stirring at room temperature for 24 h, the solutions were filtered through a silica plug in air. After washing the vial with  $\text{CH}_2\text{Cl}_2$  (3 x 1 mL), the filtrates were combined, reduced to dryness, redissolved in MeOH (10 mL) and *p*-tolylsulfonic acid (190 mg, 1.0 mmol, 0.33 equiv) added. After stirring for 24 h, a saturated aqueous solution of  $\text{KHCO}_3$  was added to quench the reaction. Upon removal of solvent, the residue was extracted with EtOAc (3 x 10 mL), filtered, concentrated and purified via column chromatography (5% EtOAc/pentane) to yield 1-undecen-4-ol (**6**) as a colorless oil.

**X-ray crystallography.** Data for **2, 3, 7, 8** and ( $^{\text{menthyl}}$ CAAC)CuMes (ESI) were collected using an Agilent Xcalibur diffractometer while those for **1, 4** and **5** were obtained using an Agilent SuperNova instrument (Table S1, ESI). All experiments were conducted at 150 K, solved using charge-flipping algorithm implemented in Olex2<sup>40</sup> and refined using SHELXL.<sup>41</sup> Refinements were largely straightforward and, hence, only points of merit will be detailed hereafter. The asymmetric unit in the structure of **1** contains two molecules. There may be some minor disorder of the NHC-carbon, in the molecule based on Cu2. This was not modelled, as attempts to do so suggest that the minor component would have had a site-occupancy of less than 10%. In **3**, the asymmetric unit comprises half of one metal complex (in which Cu1, C1 and F1 are coincident with a crystallographic 2-fold rotation axis) and one molecule of  $\text{CH}_2\text{Cl}_2$ . The latter was modelled to take account of 75:25 disorder with the addition of C-Cl bond distance restraints and some ADP restraints governing the partial occupancy chlorine atoms. There is evidence for some hydrogen bonding in the gross structure. Two, crystallographically independent molecules constitute the asymmetric unit in the structure of **5**. The moiety based on Cu1 is entirely ordered while, in the comparative Cu2 based molecule, the substituted cyclohexyl functionality based on C29 was treated for 72:25 disorder – C29 being common to both fragments. Chemically similar distances in each component were restrained to being similar in the final least-squares cycles and ADP restraints were included for atoms in the minor disordered component in order to assist convergence. There may be some disorder (in the region of 5-6%) pertaining to the Cu and F positions. This was pursued as part of the model, but ultimately abandoned because of the low level and error bars associated with site-occupancy

factors. In **7**, the hydrogen atoms attached to C42, C43 and C44 were all located and each refined at a distance of 0.98 Å from the relevant parent carbon. One cation, one anion, and one molecule of dichloromethane constitute the asymmetric unit in **8**. In the former, the apical carbon of the NHC based on C1 was disordered and modelled over two sites in an 85:15 ratio. Similarly, F2-F5 in the anion were also subject to disorder, which was modelled as two components with respective 55:45 site-occupancies. Some distance and ADP restraints were employed in disordered regions, to assist convergence.

Crystallographic data for all compounds have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1920391-1920396 for **1-5** and (<sup>menthyl</sup>CAAC)CuMes (ESI only), respectively. CCDC 1962750-1962751 contain comparative data for **7** and **8**. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details. Multinuclear NMR spectra of (carbene)CuMes and **1-8**. X-ray structure of (<sup>menthyl</sup>CAAC)CuMes.

## AUTHOR INFORMATION

### Corresponding Author

\* E-mail: m.k.whittlesey@bath.ac.uk. Tel.: 44 1225 383748

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT

We acknowledge financial support from the EPSRC Centre for Doctoral Training in Catalysis (EP/L016443/1) for JWH and the Erasmus Programme for FS. Dr Rodolphe Jazzar (UC San Diego) is thanked for the gift of [<sup>menthyl</sup>CAAC-H]BF<sub>4</sub>.

## REFERENCES

- Díez-González, S.; Marion, N.; Nolan, S. P. N-Heterocyclic carbene in late transition metal catalysis. *Chem. Rev.* **2009**, *109*, 3612-3676.
- Hahn, F. E.; Jahnke, M. C. N-Heterocyclic carbenes: Synthesis and coordination chemistry. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122-3172.
- Herrmann, W. A. N-Heterocyclic carbenes: A new concept in organometallic chemistry. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290-1309.
- Jacobsen, H.; Correa, A.; Poater, A.; Costabile, C.; Cavallo, L. Understanding the M-(NHC) (NHC = N-heterocyclic carbene) bond. *Coord. Chem. Rev.* **2009**, *253*, 687-703.
- Marion, N. NHC-Copper, silver and gold complexes in catalysis. In *N-Heterocyclic Carbenes From Laboratory Curiosities to Efficient Synthetic Tools*; Díez-González, S., Ed.; RSC Catalysis Series; RSC: Cambridge, U.K., 2011; pp 317-344.
- Pérez, P. J.; Mar Díaz-Requejo, M.; Cu, Ag, and Au-NHC Complexes in catalysis. In *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2006; pp 257-274.
- For specific examples, see: (a) Fraser, P. K.; Woodward, S. Strong ligand accelerated catalysis by an Arduengo-type carbene in copper-catalysed conjugate addition. *Tetrahedron Lett.* **2001**, *42*, 2747-2749; (b) Jurkauskas, V.; Sadighi, J. P.; Buchwald, S. L. Conjugate reduction of  $\alpha,\beta$ -unsaturated carbonyl compounds catalyzed by a copper carbene complex. *Org. Lett.* **2003**, *5*, 2417-2420; (c) Raubenheimer, H. G.; Cronje, S.; Vanrooyen, P. H.; Olivier, P. J.; Toerien, J. G. Synthesis and crystal structure of a monocarbene complex of copper. *Angew. Chem. Int. Ed.* **1994**, *33*, 672-673; (d) Tulloch, A. A. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. Structural diversity in pyridine-N-functionalized carbene copper(I) complexes. *Organometallics* **2001**, *20*, 2027-2031.
- Egbert, J. D.; Cazin, C. S. J.; Nolan, S. P. Copper N-heterocyclic carbene complexes in catalysis. *Catal. Sci. Technol.* **2013**, *3*, 912-926.
- Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. Coinage metal-N-heterocyclic carbene complexes. *Chem. Rev.* **2009**, *109*, 3561-3598.
- Lazreg, F.; Cazin, C. S. J. NHC-Copper complexes and their applications. In *N-Heterocyclic Carbenes - Effective Tools for Organometallic Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, 2014; pp 199-242.
- Lazreg, F.; Nahra, F.; Cazin, C. S. J. NHC-Copper, -silver and -gold complexes in catalysis. *Coord. Chem. Rev.* **2015**, *293-294*, 48-79.
- Boreux, A.; Marion, N.; Gagosz, F. NHC-Copper, silver and gold complexes in catalysis. In *N-Heterocyclic Carbenes From Laboratory Curiosities to Efficient Synthetic Tools* (2<sup>nd</sup> Edition); Díez-González, S., Ed.; RSC Catalysis Series; RSC: Cambridge, U.K., 2017; pp 421-455.
- Danopoulos, A. A.; Simler, T.; Braunstein, P. N-heterocyclic carbene complexes of copper, nickel and cobalt. *Chem. Rev.* **2019**, *119*, 3730-3961.
- Laitar, D. S. PhD Thesis, Massachusetts Institute of Technology, 2006.
- Fujihara, T.; Xu, T. H.; Semba, K.; Terao, J.; Tsuji, Y. Copper-catalyzed hydrocarboxylation of alkynes using carbon dioxide and hydrosilanes. *Angew. Chem. Int. Ed.* **2011**, *50*, 523-527.
- For other spectroscopically characterized examples, see: (a) Wyss, C. M.; Tate, B. K.; Bacsá, J.; Wielczko, M.; Sadighi, J. P. Dinuclear  $\mu$ -fluoro cations of copper, silver and gold. *Polyhedron* **2014**, *84*, 87-95; (b) Zhai, J. J.; Filatov, A. S.; Hillhouse, G. L.; Hopkins, M. D. Synthesis, structure, and reactions of a copper-sulfido cluster comprised of the parent Cu<sub>2</sub>S unit: {(NHC)Cu}<sub>2</sub>( $\mu$ -S). *Chem. Sci.* **2016**, *7*, 589-595.
- Suess, A. M.; Lalic, G. Copper-catalyzed hydrofunctionalization of alkynes. *Synlett* **2016**, *27*, 1165-1176.
- Suess, A. M.; Uehling, M. R.; Kaminsky, W.; Lalic, G. Mechanism of copper-catalyzed hydroalkylation of alkynes: An unexpected role of dinuclear copper complexes. *J. Am. Chem. Soc.* **2015**, *137*, 7747-7753.
- Dang, H.; Mailig, M.; Lalic, G. Mild copper-catalyzed fluorination of alkyl triflates with potassium fluoride. *Angew. Chem. Int. Ed.* **2014**, *53*, 6473-6476.
- Herron, J. R.; Ball, Z. T. Synthesis and reactivity of functionalized arylcopper compounds by transmetalation of organosilanes. *J. Am. Chem. Soc.* **2008**, *130*, 16486-16487.
- Russo, V.; Herron, J. R.; Ball, Z. T. Allylcopper intermediates with N-heterocyclic carbene ligands: Synthesis, structure and catalysis. *Org. Lett.* **2010**, *12*, 220-223.
- Herron, J. R.; Russo, V.; Valente, E. J.; Ball, Z. T. Catalytic organocopper chemistry from organosiloxane reagents. *Chem. Eur. J.* **2009**, *15*, 8713-8716.
- Zhu, G. H.; Qiu, S. N.; Xi, Y.; Ding, Y.; Zhang, D. M.; Zhang, R.; He, G. K.; Zhu, H. J. (IPr)CuF-catalyzed  $\alpha$ -site regiocontrolled trans-hydrofluorination of ynamides. *Org. Biomol. Chem.* **2016**, *14*, 7746-7753.
- Roy, M. M. D.; Ferguson, M. J.; McDonald, R.; Rivard, E. Approaching monocoordination at a silver(I) cation. *Chem. Commun.* **2018**, *54*, 483-486.
- Roy, M. M. D.; Lummis, P. A.; Ferguson, M. J.; McDonald, R.; Rivard, E. Accessing low-valent inorganic cations by using an extremely bulky N-heterocyclic carbene. *Chem. Eur. J.* **2017**, *23*, 11249-11252.
- Li, J.; Shen, W. X.; Li, X. R. Recent developments of expanded ring N-heterocyclic carbenes. *Curr. Org. Chem.* **2012**, *16*, 2879-2891.
- Melaimi, M.; Jazzar, R.; Soleilhavoup, M.; Bertrand, G. Cyclic (alkyl)(amino)carbenes (CAACs): Recent developments. *Angew. Chem. Int. Ed.* **2017**, *56*, 10046-10068.

(28) Falivene, L.; Cao, Z.; Petta, A.; Serra, L.; Poater, A.; Oliva, R. Scarano, V.; Cavallo, L. Towards the online computer-aided design of catalytic pockets. *Nat. Chem.* **2019**, *11*, 872-879.

(29) The addition of Et<sub>3</sub>N·3HF to (NHC)CuO<sup>t</sup>Bu has been used to form (NHC)CuF complexes **1-IV**. It is worth noting that in-situ formation of (NHC)CuO<sup>t</sup>Bu for a series of five-membered ring NHC, followed by addition of TREAT·HF, gave the corresponding bifluoride complexes, (NHC)Cu(FHF), rather than the fluorides. Vergote, T.; Nahra, F.; Welle, A.; Luhmer, M.; Wouters, J.; Mager, N.; Riant, O.; Leyssens, T. Unexpected copper(I) bifluoride complexes: Synthesis, characterization and reactivity. *Chem. Eur. J.* **2012**, *18*, 793-798.

(30) It is worth noting the ca. 174° and 180° C<sub>carbene</sub>-Cu-F angles in **1** and **3** respectively contrast with the corresponding C<sub>carbene</sub>-Cu-halide angles of ca. 176° (Pawar, G. M.; Bantu, B.; Weckesser, J.; Blechert, S.; Wurst, K.; Buchmeiser, M. Ring-opening metathesis polymerization-derived, polymer-bound Cu-catalysts for click-chemistry and hydrosilylation reactions under micellar conditions. *Dalton. Trans.* **2009**, 9043-9054) and 165° (ref 25) found in (6-Mes)CuCl and (ITr)CuI respectively.

(31) (6-Mes)CuO<sup>t</sup>Bu was used as we have been unable to form (ITr)CuO<sup>t</sup>Bu by reaction of (ITr)CuMes with <sup>t</sup>BuOH, presumably as a result of sterics.

(32) Yamasaki, S.; Fujii, K.; Wada, R.; Kanai, M.; Shibasaki, M. A general catalytic allylation using allyltrimethoxysilane. *J. Am. Chem. Soc.* **2002**, *124*, 6536-6537.

(33) See also: (a) Oisaki, K.; Suto, Y.; Kanai, M.; Shibasaki, M. A new method for the catalytic aldol reaction to ketones. *J. Am. Chem. Soc.* **2003**, *125*, 5644-5645. (b) Oisaki, K.; Zhao, D.; Kanai, M.; Shibasaki, M. Catalytic enantioselective aldol reaction to ketones. *J. Am. Chem. Soc.* **2006**, *128*, 7164-7165.

(34) Ibrahim, H.; Guillot, R.; Cisnetti, F.; Gautier, A. [(IPr)Cu]<sub>2</sub>(μ-OH)[BF<sub>4</sub>]: Synthesis and halide-free CuAAC catalysis. *Chem. Commun.* **2014**, *50*, 7154-7156.

(35) (a) Wyss, C. M.; Tate, B. K.; Bacsá, J.; Gray, T. G.; Sadighi, J. P. Bonding and reactivity of a μ-hydrido dicopper cation. *Angew. Chem. Int. Ed.* **2013**, *52*, 12920-12923. (b) Wyss, C. M.; Bitting, J.; Bacsá, J.; Gray, T. G.; Sadighi, J. P. Bonding and reactivity of a dicopper(I) μ-boryl cation. *Organometallics* **2016**, *35*, 71-74.

(36) For a discussion of [SiF<sub>5</sub>]<sup>-</sup> (formation and examples in d-block chemistry), see: Gorol, M.; Mösch-Zanetti, N. C.; Roesky, H. W.; Moltemeyer, M.; Schmidt, H.-G. Synthesis of a novel organoiridium fluoro complex. *Eur. J. Inorg. Chem.* **2004**, 2678-2682.

(37) Vergote, T.; Nahra, F.; Peeters, D.; Riant, O.; Leyssens, T. NHC-copper(I) bifluoride complexes: 'Auto-activating' catalysts. *J. Organomet. Chem.* **2013**, *730*, 95-103.

(38) Collins, L. R.; Riddlestone, I. M.; Mahon, M. F.; Whittlesey, M. K. A comparison of the stability and reactivity of diamido- and diaminocarbene copper alkoxide and hydride complexes. *Chem. Eur. J.* **2015**, *21*, 14075-14084.

(39) Hall, J. W.; Unson, D. M. L.; Brunel, P.; Collins, L. R.; Cybulski, M. K.; Mahon, M. F.; Whittlesey, M. K. Copper-NHC-mediated semihydrogenation and hydroboration of alkynes: Enhanced catalytic activity using ring-expanded carbenes. *Organometallics* **2018**, *37*, 3102-3110.

(40) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339-341

(41) Sheldrick, G. M. *Acta. Cryst.* **1990**, *467-473*, A46. Sheldrick, G. M. SHELXL-97, a computer program for crystal structure refinement, University of Göttingen, 1997.

## TOC entry

